



# Boosting strong metal-support interactions between Ru and sodium titanate nanowire for hydrogenolysis of polyolefins under mild conditions

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## ABSTRACT

Catalytic hydrogenolysis provides promising opportunities for the chemical recycling of polyolefins. In this study, we have successfully developed a novel catalyst consisting of ruthenium (Ru) nanoparticles supported on sodium titanate nanowires (Ru@NTO-NH) for the hydrogenolysis of low-density polyethylene (LDPE) into high-value long-chain alkanes under mild reaction conditions (180 °C, 1–2 MPa H<sub>2</sub>), achieving yields of up to 91%. Control experiments and thorough characterizations have elucidated that the exceptional catalytic performance of Ru@NTO-NH in the hydrogenolysis of polyolefins can be attributed to strong metal-support interactions (SMSI). NTO-NH exhibits stronger SMSI with Ru species than TiO<sub>2</sub>, leading to the formation of smaller Ru nanoparticles that are more positively charged and NaTiO<sub>3</sub>-overlayered. This unique configuration facilitates the adsorption and activation of H<sub>2</sub> as well as the desorption of alkanes, thereby enhancing catalytic efficiency and selectivity towards liquid alkanes. Moreover, the Ru@NTO-NH catalyst demonstrates remarkable stability throughout recycling experiments (10 runs). Notably, apart from LDPE, high-density polyethylene (HDPE) and polypropylene (PP) can also be effectively converted into liquid alkanes through hydrogenolysis using this catalyst.

## 1. Introduction

Polyolefin is the most widely used type of plastics, accounting for approximately 57% of the total plastic production worldwide. It has been found that polyolefin plastics can persist in the soil environment for over 400 years [1]. Therefore, the degradation of polyolefins is a critical aspect of plastic control [2]. Currently, more than 70% of plastic waste is disposed of in landfills, nature, or incinerated, which pose a significant threat to the environment [3]. Consequently, the development of efficient, cost-effective, and environmentally friendly strategies for degrading waste polyolefin plastics has become a major research focus in the field of plastic management [4]. Chemical recycling offers considerable advantages over landfilling, incineration, and biodegradation methods, as it enables the conversion of waste plastics into value-added chemicals within a short timeframe [5]. In the context of polyolefins, chemical degradation and recovery technologies primarily involve two main approaches: pyrolysis and catalytic hydrogenolysis. High temperature pyrolysis can depolymerize polyolefins by breaking strong C-C bonds in them, producing small molecules [6]. However,

these processes are energy intensive and offer low control over product selectivity [7]. Alternatively, selective depolymerization of polyolefins into liquid alkanes with target molecular weight range by catalytic hydrogenolysis of C-C bonds has been popular research recently [8]. The development of efficient and sustainable methods for the degradation of polyolefin plastics is crucial for effective plastic management. Chemical recycling, particularly through catalytic hydrogenolysis, holds promise for converting waste polyolefins into valuable chemicals, offering an alternative to conventional disposal methods.

Recent reports have shown that noble metal ruthenium nanoparticles deposited on silica, alumina, ceria, niobium, tungsten oxide, zirconia, zeolite or carbon in the presence of H<sub>2</sub> can easily break C-C bonds in the polyolefin backbone via hydrogenolysis and produce low molecular-weight wax or fuel-range hydrocarbons. For example, supported Ru catalysts such as Ru/C [9], Ru/CeO<sub>2</sub> [10], Ru/WZrO<sub>x</sub> [11], Ru/TiO<sub>2</sub> [12], displayed good catalytic performance for hydrogenolysis of polyolefin. Although great progress has been made rapidly, the main drawback of Ru-based catalysts is its strong tendency to break terminal C-C bonds, which results in forming low-value methane and other light

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alkanes [9d,10b,13]. In addition, most Ru-catalyzed hydrogenolysis of polyolefins also encounter some issues, such as harsh reaction conditions ( $T > 250\text{ }^{\circ}\text{C}$ ,  $\text{H}_2$  pressure  $> 3\text{ MPa}$ ), poor catalyst recovery. Hence, the exploration of high-performance Ru catalysts to achieve selective hydrogenolysis of polyolefin plastics under mild reaction conditions is appealing and significant.

To date, it has been found that the support type has a great influence on the performance of Ru catalysts for hydrogenolysis of polyolefins, but only few reports address this crucial observation [9]. For example, Tomishige's group disclosed that Ru/CeO<sub>2</sub> has better catalytic activity and selectivity than other metal oxide supported Ru catalysts, because the basic property of CeO<sub>2</sub> is beneficial to the dispersion of Ru species [10b]. The Vlachos's group proposed a facile method to regulate the metal support interaction (MSI) in Ru/TiO<sub>2</sub>, and demonstrated that the stronger MSI can improve the ability of Ru NPs to adsorb and activate H<sub>2</sub>, thereby promote the hydrogenolysis of polyolefins [12b]. The Pérez-Ramírez's team proposed that the TiO<sub>2</sub> crystal phase type is related to the degree of the strong metal-support interaction (SMSI), which ultimately affects PE hydrogenolysis [12c]. It is well known that SMSI has a strong impact on the activity and selectivity of heterogeneous catalysts [14,15]. However, there are a handful of studies on improving the efficiency of polyolefin hydrogenolysis by SMSI modification, mainly focusing on TiO<sub>2</sub>-supported Ru-based catalysts [12b,12c]. Thus, the possibility of other supported catalysts with SMSI in polyolefin hydrogenolysis still needs to be further explored.

Herein, a newly developed sodium titanate nanowire supported ruthenium catalyst (Ru@NTO-NH) has been disclosed. LDPE can be selectively converted to high-value long-chain alkanes ( $\geq \text{C}_6$ ) at  $180\text{ }^{\circ}\text{C}$  and  $1\text{ MPa H}_2$  with excellent recovery performance. The catalyst also shows excellent catalytic performance for the hydrolysis of other commonly used polyolefin plastics in life, such as PE plastic bag and PP bottle. Further characterization and experiments suggest that the SMSI between Ru and NTO can be adjustable by controlling the calcination conditions, which plays a significant role in the catalytic performance for polyolefin hydrogenolysis.

## 2. Experimental sections

### 2.1. Catalyst preparation

**Synthesis of sodium titanate nanowires (NTO) and hydrogen titanate nanowires (HTO):** The synthesis approach refers to the preparation process in the literature [16]. In a typical synthesis,  $1.2\text{ g}$  of TiO<sub>2</sub> powder was dispersed in  $60\text{ mL}$  of NaOH ( $10\text{ M}$ ) solution, stirred continuously until the dispersion was uniform, and then transferred to a  $100\text{ mL}$  stainless steel autoclave, which was placed in an oil bath at

slowly dripped to NTO dispersion. At room temperature, stirring for  $2\text{ h}$ , then slowly dripping  $25\text{ mL NaBH}_4$  aqueous solution ( $60\text{ mmol/L}$ ) into the mixture, reducing for  $2\text{ h}$ . Then the precursor Ru@NTO was obtained by spinning and drying. The precursors were pretreated at  $400\text{ }^{\circ}\text{C}$  for  $2\text{ h}$  in  $\text{N}_2$  atmosphere, and then Ru@NTO-N was obtained by natural cooling. Ru@NTO-NH was obtained by vacuum drying after washing and roasting at  $450\text{ }^{\circ}\text{C}$  for  $3\text{ h}$  in  $5\text{ vol\% H}_2/\text{Ar}$  atmosphere. Ru@NTO-H was obtained by direct reduction of the precursor at  $450\text{ }^{\circ}\text{C}$  for  $3\text{ h}$  in  $\text{Ar/H}_2$  atmosphere. During the preparation of Ru@NTO-NH, the amount of Ru added was  $5\text{ wt\%}$ , and the content of Ru in Ru@NTO was about  $5.1\text{ wt\%}$  measured by ICP-MS (Table S1).

The synthesis of other Ru/supports (TiO<sub>2</sub>, WO<sub>3</sub>, CeO<sub>2</sub>, MgO,  $\gamma\text{-Al}_2\text{O}_3$ , HTO) catalysts is the same as that of Ru@NTO-NH catalysts except for the replacement of supports. The synthetic procedures of Ru/NTO-NH are the same with that of Ru@NTO-NH, with the exception that the NaBH<sub>4</sub> reduction process is not included in the preparation process.

### 2.2. Catalytic activity tests

The typical procedure for hydrogenolysis of LDPE on Ru@NTO-NH is as follows, and the activity test is carried out in a  $30\text{ mL}$  stainless steel autoclave reactor. LDPE ( $500\text{ mg}$ ) and Ru@NTO-NH ( $100\text{ mg}$ ) were put into stainless steel autoclave reactor, whose interior is a slender cylinder with a small bottom area of about  $2\text{ cm}^2$ . After feeding, the catalyst and LDPE were thoroughly mixed by mechanical grinding, then assemble the stainless-steel autoclave reactor, and adding a small cylindrical rotor. After sealing, the reactor was purged with H<sub>2</sub> for  $6$  times and pressurized to  $1\text{ MPa}$  with H<sub>2</sub>, then put into a preheated heating device. The reactor was heated to  $180\text{ }^{\circ}\text{C}$  at the stirring speed of  $600\text{ rpm}$  and reacted for  $8\text{ h}$ . The melting point of LDPE is  $108\text{--}126\text{ }^{\circ}\text{C}$ , and the reaction takes place at  $180\text{ }^{\circ}\text{C}$ , where the raw material also serves as the solvent.

After the end of the reaction, the components in the kettle were cooled and collected for analysis. The liquid phase products are dissolved in dichloromethane, filtered and separated from the solid liquid phase, and the solid phase is dried and weighed (Fig. S1). The dichloromethane in the liquid product was dried and weighed, and the conversion and liquid selectivity were calculated. The quantitative 9,10-dihydroanthracene was added to the liquid phase as the internal standard, which was diluted to a certain concentration with quantitative dichloromethane, and the component selectivity of the liquid product was analyzed by gas chromatography. The maximum carbon number which can be analyzed by GC-FID is  $35$  due to high boiling point of products, and product distribution was decided as follows: gas (C1-C5), liquid fuel (C6-C21), wax (C22-C35). The conversion and yield were calculated with the formulas shown below:

$$\text{Conversion}[\%] = \left( \frac{\text{Amount of substrate input}[\text{g}] - \text{Amount of unreacted substrate}[\text{g}]}{\text{Amount of substrate input}[\text{g}]} \right) \times 100$$

$130\text{ }^{\circ}\text{C}$ , stirring for  $24\text{ h}$  (the stirring speed affects the morphology of the nanowires, and the stirring speed remains unchanged each time). After the reaction, the autoclave was removed from the oil bath and cooled to room temperature. The product sodium titanate (NTO) was collected by centrifugation, washed  $6$  times with deionized water, and then air-dried at  $80\text{ }^{\circ}\text{C}$  to obtain a sodium titanate nanowire material.

HCl aqueous solution ( $1\text{ M}$ ,  $10\text{ mL} \times 2$ ) is employed for washing NTO ( $1\text{ g}$ ) twice to exchange  $\text{Na}^+$ , followed by deionized water until neutral. The solid obtained through filtration is HTO.

**Synthesis of Ru@NTO-X (X = N, H, NH):** The catalyst was prepared by impregnation approach.  $300\text{ mg}$  NTO was dispersed in  $30\text{ mL}$  deionized water, and  $25\text{ mL RuCl}_3$  aqueous solution ( $6\text{ mmol/L}$ ) was

$$\text{Liquid phase yield}[\%] = \frac{\text{Liquid phase product content}[\text{g}]}{\text{Amount of substrate added}[\text{g}]} \times 100$$

$$\text{Gas yield}[\%] = \text{Conversion}[\%] - \text{Liquid phase yield}[\%]$$

$$\text{Selectivity}[\% - \text{C}] = \frac{\text{Amount of each products}[\text{mol} - \text{C}]}{\sum \text{Amount of product}[\text{mol} - \text{C}]} \times 100$$

$$\text{Yield}[\% - \text{C}] = \text{Conversion}[\%] \times \text{Selectivity}[\% - \text{C}] \times 100$$

The residual solids collected after the reaction is assumed to be unreacted substrates and catalysts, although unreacted substrates could

partially react. The amount of unreacted substrate is estimated according to the following equation: the unreacted substrate (g) = (the residual solid weight (g)) - (the introduced catalytic amount (g)), and the experimental error is within the range of  $\pm 10\%$ .

### 2.3. Characterization methods

X-ray diffraction (XRD) analysis was conducted using a Shimadzu X-ray diffractometer (XRD-6000) with Cu K $\alpha$  irradiation. Transmission electron microscopy (TEM) images were captured utilizing a PHILIPS Tecnai 12 microscope operating at 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images at atomic resolution were obtained using a FEI Titan Cubed Themis G2 300 S/TEM equipped with a probe corrector and a monochromator, operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer, employing an Al K $\alpha$  X-ray source (1350 eV) and calibrated by referencing the C 1 s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was conducted on an Optima 7300 DV instrument. BET surface area and pore size measurements were carried out using N<sub>2</sub> adsorption/desorption isotherms at 77 K, employing a Micromeritics ASAP 2020 instrument. Prior to measurements, the samples were degassed at 150 °C for 12 h. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectra were recorded using a Bruker Equinox 55 spectrometer. For CO adsorption measurements, the sample underwent in-situ pretreatment with H<sub>2</sub> at 450 °C for 1 h, followed by cooling to 25 °C. The gas flow was then switched to He and maintained at this temperature for 0.5 h before collecting the background spectrum. Subsequently, 5 vol% CO/He was introduced until saturation of CO adsorption was achieved. The system was then purged with He to remove gaseous CO, after which the CO-DRIFT spectrum was collected in Kubelka-Munk mode. Temperature-programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR) was performed using a Micromeritics AutoChem II 2920 instrument. For H<sub>2</sub>-TPR. The sample was subjected to a 1 h pretreatment with Ar at 300 °C, followed by cooling to 100 °C. Subsequently, the sample underwent a 30 min purging step with an inert gas at 100 °C. Finally, a 10 vol% H<sub>2</sub>/Ar mixture was introduced into the system, and the temperature was increased from 100 °C to 800 °C using a heating rate of 10 °C/min. For temperature-programmed desorption of H<sub>2</sub> (H<sub>2</sub>-TPD) analysis, the sample was pre-reduced in a 60-sccm flow of 5% H<sub>2</sub> mixed with He at 523 K for 1 h. It was then cooled to room temperature and purged with a 60-sccm flow of He gas for at least 1 h to stabilize the baseline of the H<sub>2</sub> mass spectrometry (MS) signal. Subsequently, H<sub>2</sub>-TPD measurements were conducted using the same ramping program. The MS signal was calibrated using a MicroGC (990 MicroGC, Agilent) equipped with an MS5A column. The MS signal of He was used as a semi-quantitative internal reference for H<sub>2</sub> adsorption/desorption. Butane-TPD was performed in a quartz tube reactor, and the exhaust gas was

analyzed using an HIDEN HPR20 online mass spectrometer. The experimental procedure was similar to that of H<sub>2</sub>-TPD, with the exception that butane vapor was introduced instead of H<sub>2</sub> into the catalyst with Ar flow at room temperature. The temperature was increased from 30 °C to 800 °C at a rate of 10 °C/min, and the MS signal of  $m/z = 58$  (butane) was continuously recorded. Raman spectra were acquired on a Horiba HR evolution spectrometer using a 532 nm green laser (5 mW power),  $\times 50$  objective, and 1800 g/mm grating. The detector resolution under these conditions is approximately 0.48 cm<sup>-1</sup>/pixel. O<sub>2</sub> temperature-programmed oxidation (O<sub>2</sub>-TPO) was conducted in a 10% O<sub>2</sub>/Ar flow, raising the temperature from 30 °C to 800 °C at a rate of 15 °C/min. Electron paramagnetic resonance (EPR) measurements were performed on a Bruker A300 EPR EMX Nano Spectrometer at 77 K.

### 3. Results and discussion

As shown in Fig. 1, TiO<sub>2</sub> reacts with NaOH to grow NTO by mechanical stirring in a hydrothermal setup [16]. Ru@NTO is prepared by an impregnation-reduction method. The use of NaBH<sub>4</sub> in the impregnation process is for effective adsorption Ru species in the support (Fig. S2). Ru is impregnated on the support of NTO and calcinated under N<sub>2</sub> or H<sub>2</sub> atmosphere to produce Ru@NTO-N and Ru@NTO-H, respectively. The catalyst obtained after both N<sub>2</sub> calcination and H<sub>2</sub> reduction is named Ru@NTO-NH. As a comparison, Ru/TiO<sub>2</sub>, Ru/HTO-NH was also prepared with the similar procedures of Ru@NTO-NH.

NTO exhibits a nano hollow wire structure, which is consistent with the literature results (Fig. S3a) [16]. The doping of Ru does not significantly change the morphology of NTO (Fig. 2a). Further calcination increases the crystallinity of NTO (Figs. 2c-e), which is broken into shorter nanowires (Fig. S3a vs S3b). The HAADF-STEM images and EDS mapping results proved that Ru was loaded on NTO in the form of nanoparticles (Fig. S3c and S3d) and the Ru NPs with average size about 1.95 nm are uniform dispersed in Ru@NTO-NH (Fig. 2f). Although Ru NPs are also homogeneously distributed on the surface of polygonal TiO<sub>2</sub> particles, its average particle size is larger than that over Ru@NTO-NH (3.10 nm vs 1.95 nm) (Figs. 2g,h). The formation of small-sized Ru nanoparticles on NTO might be due to the introduction of alkali sites and larger specific surface area [17].

The specific surface area and pore volume of Ru@NTO-NH were 40.7 m<sup>2</sup>/g and 0.2 cm<sup>3</sup>/g, respectively, which are higher than those of Ru/TiO<sub>2</sub> (21.6 m<sup>2</sup>/g and 0.1 cm<sup>3</sup>/g) (Fig. S4, Table S2). Therefore, NTO with larger specific surface area can provide more area in contact with the reactants than TiO<sub>2</sub> and can expose more active Ru sites. The BET specific surface area of Ru@NTO-NH is smaller than that of Ru@NTO (64.6 m<sup>2</sup>/g) since high-temperature calcination damages the structure of NTO, causing its aggregation.

XRD characterization of the NTO reveals the presence of several crystalline phases and amorphous components. The main diffraction

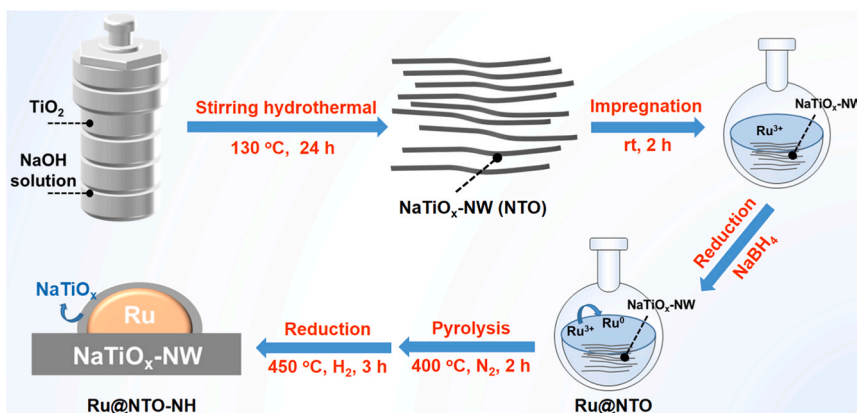
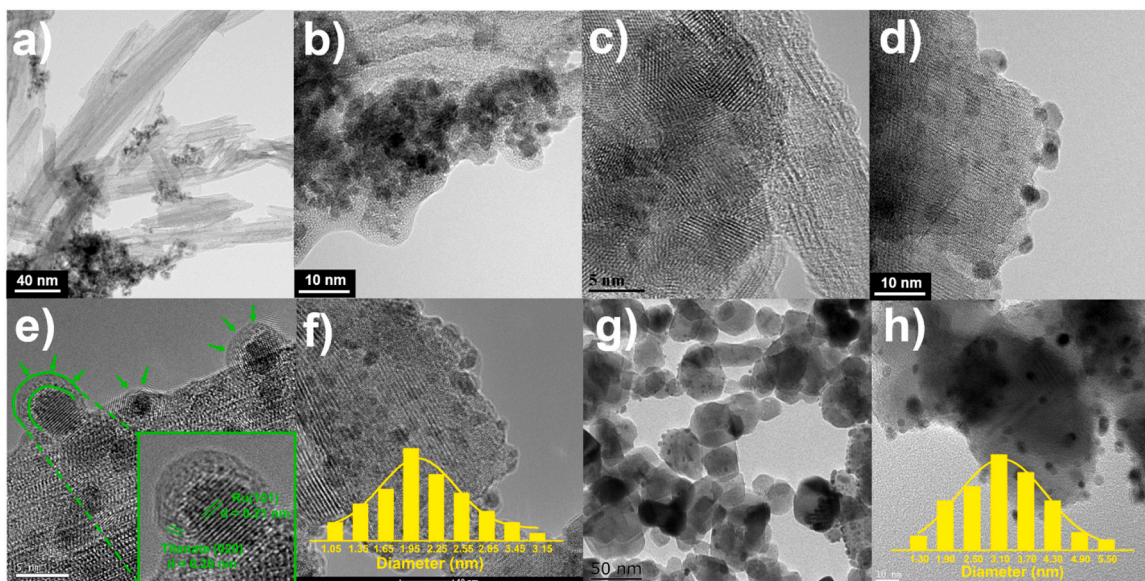


Fig. 1. The synthesis strategy of Ru@NTO-NH.



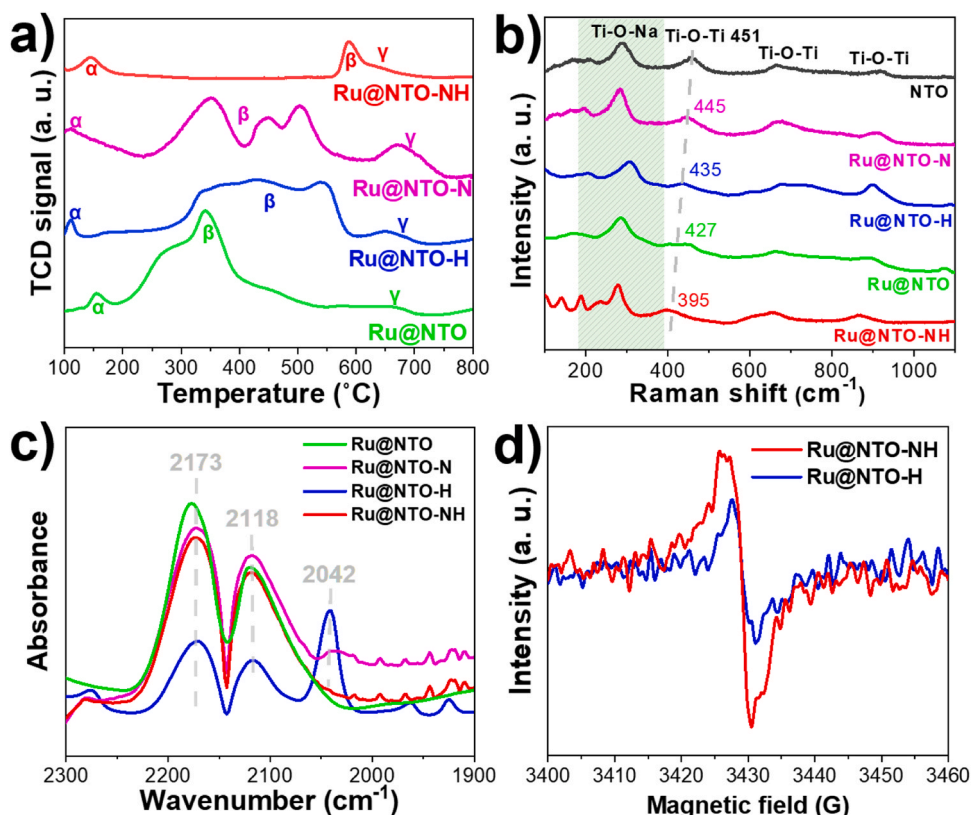


**Fig. 2.** (a) TEM and (b) HRTEM images of Ru@NTO; HRTEM images of (c) Ru@NTO-N, (d) Ru@NTO-H, (e, f) Ru@NTO-NH; (g) TEM and (h) HRTEM images of Ru/TiO<sub>2</sub>. The Ru loading of the above materials is 5 wt%.

peaks can be attributed to the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, Na<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>, Na<sub>2</sub>Ti<sub>9</sub>O<sub>19</sub>, and Na<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> crystalline phases, while the remaining peaks may correspond to amorphous components. The diffraction peaks of Ru species (including Ru and RuO<sub>2</sub>) are not detected in both XRD patterns of Ru@NTO-NH and Ru/TiO<sub>2</sub>, indicating a high dispersion of Ru material on the support [18] (Fig. S5), which is consistent with the HRTEM results.

The morphology of the catalyst interface was further investigated. The Ru NPs were encapsulated by the NTO-derived NaTiO<sub>x</sub> overlayers

with a thickness of ~1.25 nm (Fig. 2e). The crystal plane spacing of 0.21 nm and 0.20 nm was measured and assigned to the (101) plane of metallic Ru and the (020) plane of orthorhombic titanate crystal structure [16a,19]. In addition, the loaded Ru NPs were partially encapsulated by TiO<sub>x</sub> overlayers (Fig. 2e). In order to understand the process for the formation of the NaTiO<sub>x</sub> overlayers between Ru and NTO, five NTO-supported Ru catalysts prepared by different conditions were detected by HRTEM. It is observed that NaTiO<sub>x</sub> also wraps around Ru NPs in the Ru@NTO (Fig. 2b). After N<sub>2</sub> calcination, the crystallinity of



**Fig. 3.** Spectra of (a) H<sub>2</sub>-TPR, (b) Raman, (c) CO-adsorption FT-IR and (d) EPR profiles. The Ru loading of the above materials is 5 wt%.



NTO is improved (Fig. 2c). The distribution of Ru species is poor in both Ru@NTO and Ru@NTO-N catalysts (Fig. S6a and S6b). In contrast to Ru@NTO and Ru@NTO-N catalysts, Ru NPs are more dispersed in Ru@NTO-H and Ru@NTO-NH catalysts containing cladding layers (Figs. 2d,e and S5c), which is attributed to the anchoring of the metal by the NaTiO<sub>x</sub> overlayers [20]. Obvious aggregation of Ru particles is observed in the case of Ru@NTO-NH, and there is no overlayer on the Ru particles (Fig. S6d), so the NaBH<sub>4</sub> reduction step is necessary for the formation of SMSI.

In order to clarify the SMSI effect between Ru NPs and NTO, we first analyzed the reducibility of ruthenium metal on the catalyst by temperature-programmed reduction (TPR) analysis. According to H<sub>2</sub> temperature-programmed reduction (TPR) results (Fig. 3a), there are three main reduction features at 100–200 °C ( $\alpha$ ), 200–600 °C ( $\beta$ ) and 600–700 °C ( $\gamma$ ). The low-temperature feature peak ( $\alpha$ ) corresponds to the reduction of surface RuO<sub>x</sub> [15a]. The feature peak ( $\beta$ ) is mainly attributed to the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> in NTO [20]. The feature peak ( $\gamma$ ) belongs to the reduction of Ru species that interacted strongly with the support [21]. The characteristic peaks in the range of 200–600 °C ( $\beta$ ) are not only related to Ti<sup>3+</sup> and the oxygen vacancy [22], but also to the specific surface area and material structure, so it is unable to determine the number of Ti<sup>3+</sup> and oxygen vacancies in these catalysts based on H<sub>2</sub>-TPR results. Compared to Ru@NTO-NH, the lower temperature range and the wider feature peaks ( $\beta$ ) of Ru@NTO, Ru@NTO-N and Ru@NTO-H can be attributed to their loose crystal structure and the presence of Na<sup>+</sup>, which makes NTO easier to be reduced [15a,20].

The Raman spectra also prove the existence of SMSI (Fig. 3b), the characteristic peaks below 400 cm<sup>-1</sup> can be attributed to surface Ti-O-Na vibration, and adsorption band above 400 cm<sup>-1</sup> can be interpreted as Ti-O-Ti crystal phonons [23]. The Ti-O-Ti characteristic signals red-shifted in these samples compared with NTO, indicating that (1) there are SMSI between NTO and Ru NPs; (2) the SMSI may be enhanced by N<sub>2</sub> calcination and H<sub>2</sub> reduction; (3) the SMSI become stronger in order of Ru@NTO-NH > Ru@NTO > Ru@NTO-H > Ru@NTO-N [24].

These NTO-supported Ru catalysts were further characterized by CO-adsorption FT-IR and XPS to confirm the SMSI effects. The CO adsorbed on Ru@NTO-H exhibits obvious bands at 2173, 2118, and 2042 cm<sup>-1</sup> (Fig. 3c), which are attributed to the CO adsorption on NTO [12b], partially oxidized Ru<sup>n+</sup> and Ru<sup>0</sup>, respectively [25]. According to HRTEM and XPS results (Figs. 2d and 4a), there are more Ru<sup>0</sup> sites exposed on the surface of Ru@NTO-H, so the CO adsorption peak at 2042 cm<sup>-1</sup> is more significant. There is no obvious CO adsorption signal at 2042 cm<sup>-1</sup> in the cases of Ru@NTO, Ru@NTO-N and Ru@NTO-NH owing to the existence of denser NaTiO<sub>x</sub> overlayer (Figs. 2b, c and e), which inhibits the reduction of Ru sites on the catalyst surface, resulting in fewer Ru<sup>0</sup> sites on the catalyst surface (Fig. 4a) [12c]. There are still strong CO adsorption signals at NTO and Ru<sup>n+</sup> sites on the surfaces of these

catalysts (Ru@NTO, Ru@NTO-N and Ru@NTO-NH). Therefore, the NTO-derived overlayer will not inhibit CO adsorption.

The oxygen vacancy can enhance the CO adsorption on NTO (2173 cm<sup>-1</sup>) [26], which not only related to the oxygen vacancy, but also to the specific surface area, morphology, surface charge and other factors. Thus, it is unable to determine the number of oxygen vacancies in these catalysts based on CO-adsorption FT-IR results. The electron paramagnetic resonance (EPR) was also performed to confirm oxygen vacancy and the SMSI strength (Fig. 3d). The EPR signal of Ru@NTO-NH is stronger than that of Ru@NTO-H, indicating that there are more oxygen vacancies and Ti<sup>3+</sup> species on the surface of catalysts, suggesting Ru@NTO-NH contains more notable SMSI [27].

The chemical composition of the surface and the states of Ti, Na, Ru over the Ru/TiO<sub>2</sub> and Ru@NTO-NH were studied by XPS (Figs. 4a and b). In comparison with Ru/TiO<sub>2</sub>, the Ru 3d<sub>5/2</sub> peak of Ru@NTO-NH shifted to a higher binding energy, indicating that Ru@NTO-NH has more electron-deficient Ru NPs than Ru/TiO<sub>2</sub> since the NaTiO<sub>x</sub> overlayers may inhibit the reduction of Ru NPs [20]. The peaks of Na 1s and Ti 2p move higher binding energy after the loading of Ru, suggesting that there was electron transfer from NTO to Ru NPs (Figs. 4b and c) [15a]. The signal peaks of Ti 2p and Na 1s shift towards lower binding energy in the order of Ru@NTO-H, Ru@NTO, and Ru@NTO-NH, indicating that the doping of alkali metals and more incompletely coordinated Ti<sup>3+</sup> cations and oxygen vacancies on the Ru@NTO-NH catalyst [15a,28]. Among them, the Ti 2p<sub>3/2</sub> peak deconvolutes to two peaks at around 458.6 and 458.1 eV, corresponding to Ti<sup>4+</sup> and Ti<sup>3+</sup>, respectively. The ratio of the Ti<sup>3+</sup> peak increases gradually in the aforementioned order (Table S3). The binding energy order of Ru 3d signal is opposite to Na 1s. Ru exists in the mixed states of metal state (Ru<sup>0</sup>) and positively charged state (Ru<sup>n+</sup>). The ratio of Ru<sup>n+</sup>/Ru<sup>0</sup> is 1.59 (Ru@NTO-NH), 1.13 (Ru@NTO) and 0.75 (Ru@NTO-H), respectively (Fig. 4a and Table S4), indicating that Ru@NTO-NH are more electron deficient.

In accordance with the above results, the formation mechanism of different NTO supported Ru catalysts was illustrated in Fig. 5. A small amount of free TiO<sub>2</sub> will be adsorbed on the surface of Ru NPs during the impregnation reduction process. NaTiO<sub>x</sub>-coating is different with TiO<sub>x</sub>-coating, because it will be weakened under H<sub>2</sub> calcination conditions [15a]. The N<sub>2</sub> calcination enhances the crystallinity of the catalyst [29], which can avoid the incomplete overlayer caused by over-excessive reduction of NaTiO<sub>x</sub> coating in the H<sub>2</sub> reduction process. H<sub>2</sub> reduction can make the dispersion of Ru species more evenly in the support and weaken the NaTiO<sub>x</sub> coating of Ru NPs.

To further elucidate the role of the unique SMSI overlayers over the interface of Ru@NTO-NH, we performed hydrogen temperature programmed desorption (H<sub>2</sub>-TPD) experiments on Ru/TiO<sub>2</sub> and Ru@NTO-NH (Fig. 6a, Table S5). The desorption peak at 89 °C of Ru@NTO-NH and 151 °C of Ru/TiO<sub>2</sub> can be attributed to the H<sub>2</sub> desorption on the

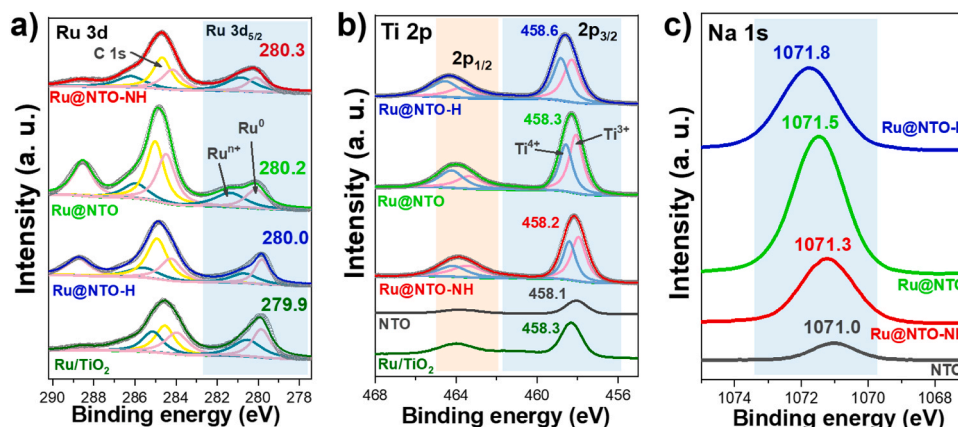


Fig. 4. (a) Ru 3d (b) Ti 2p and (c) Na 1s XPS spectra of NTO, Ru@NTO, Ru@NTO-H, Ru/TiO<sub>2</sub> and Ru@NTO-NH. The Ru loading of the above materials is 5 wt%.

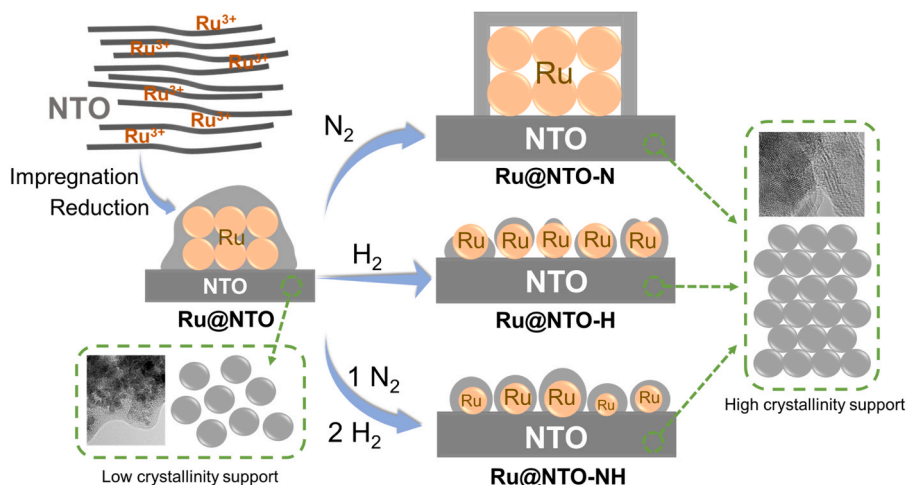


Fig. 5. The formation mechanism of different NTO supported Ru catalysts.

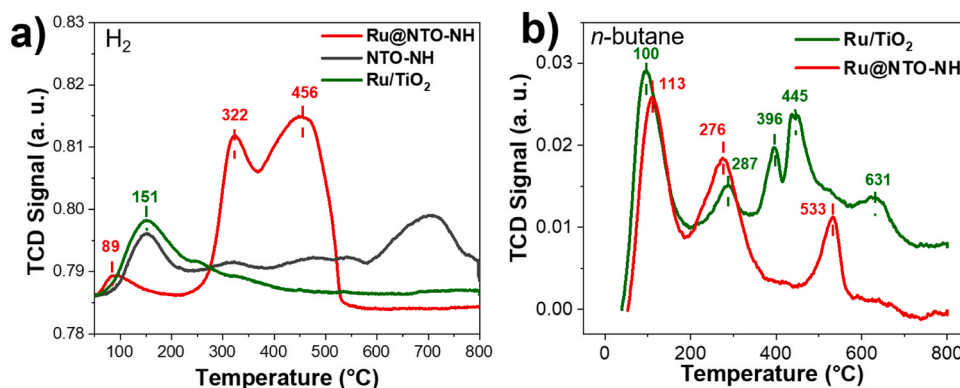


Fig. 6. (a)  $H_2$ -TPD and (b)  $n$ -butane-TPD profiles of  $Ru/TiO_2$  and  $Ru@NTO-NH$ .

$Ru$  adsorption site [30]. The large desorption peaks of  $Ru@NTO-NH$  at high temperatures (322 °C and 456 °C) are correlated to the reverse hydrogen spillover from NTO to  $Ru$  [15a,31]. It is worth noting that there are obvious  $H_2$  desorption peaks in the  $H_2$ -TPD of NTO-NH, indicating that  $H_2$  can be adsorbed on the NTO. Therefore,  $Ru@NTO-NH$  has better  $H_2$  activation ability and higher  $H^*$  coverage than  $Ru/TiO_2$ . Butane-TPD tests were performed to investigate the affinities of the  $Ru/TiO_2$  and  $Ru@NTO-NH$  to alkanes (Fig. 6b, Table S6). Compared with  $Ru/TiO_2$ ,  $Ru@NTO-NH$  has higher butane desorption rate and

amount, suggesting that the  $NaTiO_x$  overlayers weakens the interactions between  $Ru$  NPs and alkyl chains, facilitating the desorption of alkyl chains.

The catalytic activity of different metal oxides supported  $Ru$  catalysts were investigated for LDPE hydrogenolysis reaction (Fig. 7a, Table S7). The catalytic activity for LDPE hydrogenolysis follows the order of  $Ru/TiO_2 > Ru/\gamma-Al_2O_3 > Ru/CeO_2 > Ru/MgO > Ru/WO_3$ . The LDPE hydrogenolysis activity over  $Ru/TiO_2$  catalyst reaches 79%, but liquid alkane selectivity is poor (46%). The catalytic performance of NTO

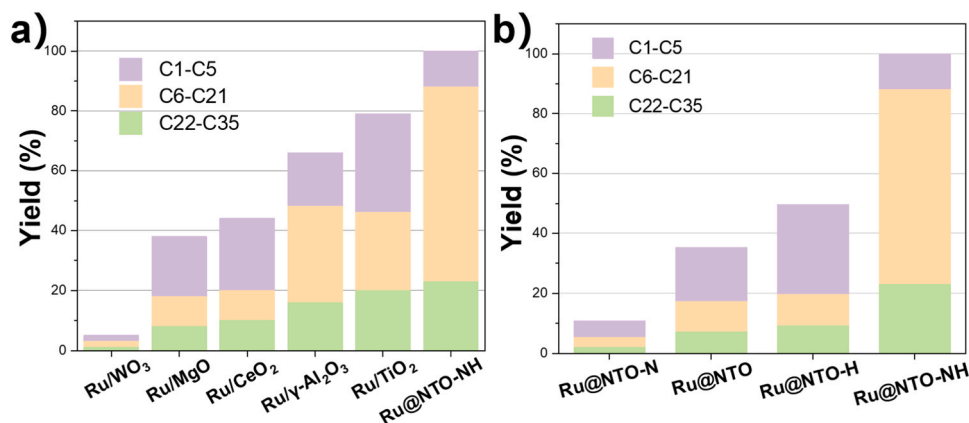


Fig. 7. (a) Yield distribution of LDPE hydrogenolysis over different supported  $Ru$  catalysts. (b) Yield distribution of LDPE hydrogenolysis catalyzed by NTO supported  $Ru$  catalysts. Reaction conditions: LDPE (500 mg), 5 wt%  $Ru$  Cat. (100 mg), 180 °C, 8 h, 1 MPa  $H_2$ .

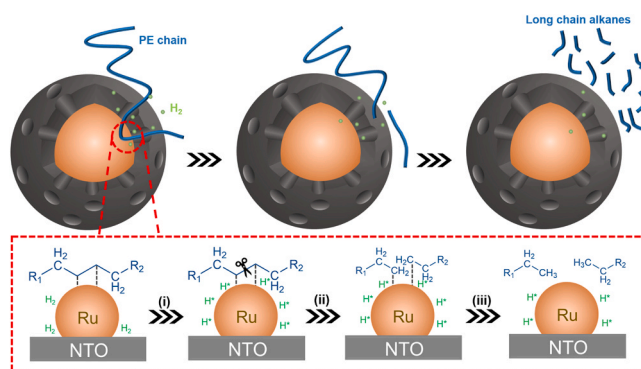
supported Ru catalysts on the LDPE hydrogenolysis was also studied (Fig. 7b, Table S8, entries 1–4). The catalytic activity for LDPE hydrogenolysis is in the order of  $\text{Ru@NTO-NH} > \text{Ru@NTO-H} > \text{Ru@NTO} > \text{Ru@NTO-N}$ .  $\text{Ru@NTO-NH}$  exhibits excellent LDPE hydrogenolysis activity and liquid alkane selectivity. The distribution of liquid products was analyzed by GC-MS (Fig. S7). Obvious aggregation of Ru NPs is observed in the cases of  $\text{Ru@NTO}$  and  $\text{Ru@NTO-N}$ , so both of them exhibits poor catalytic activity on the LDPE hydrogenolysis. In comparison of  $\text{Ru@NTO-NH}$ ,  $\text{Ru@NTO-H}$  contains more electron-rich Ru NPs whose have incomplete  $\text{NaTiO}_x$ -overlayer, so it exhibits poor catalytic activity and liquid alkane selectivity for LDPE hydrogenolysis.

In view of  $\text{N}_2$  possible activation effects on Ru,  $\text{Ru@NTO-ArH}$  prepared by calcination under Ar is used for the hydrogenolysis of LDPE. The experimental results are roughly consistent with  $\text{Ru@NTO-NH}$  (Table S8, entry 5). The catalytic efficiency of  $\text{Ru/HTO-NH}$  is significant decrease, with only 31% conversion obtained under the same conditions (Table S8, entry 6). Therefore, the presence of  $\text{Na}^+$  can effectively improve the performance of the catalyst, since  $\text{Na}^+$  can also provide more base sites of catalysts, which is beneficial for the uniform dispersion of Ru species [17]. The conversion of  $\text{Ru/NTO-NH}$  hydrogenolysis LDPE decreased to 5% (Table S8, entry 7), so that the  $\text{NaBH}_4$  reduction step is crucial to improve the catalytic activity of the catalyst.

According to structural characterization data, the excellent performance of  $\text{Ru@NTO-NH}$  can be attributed to prominent SMSI between Ru and NTO, thereby leading to smaller, more positively charged Ru NP coated by  $\text{NaTiO}_x$ .  $\text{Ru@NTO-NH}$  contains smaller and more positively charged Ru NPs than other Ru catalysts ( $\text{Ru/TiO}_2$ ,  $\text{Ru@NTO}$ ,  $\text{Ru@NTO-N}$  and  $\text{Ru@NTO-H}$ ) (detected by TEM and XPS) (Fig. 2 and Fig. 4), which is conducive to  $\text{H}_2$  activation and  $\text{H}^*$  coverage (confirmed by  $\text{H}_2$ -TPD), thereby improving the catalytic activity and selectivity [10a,12b]. Furthermore, the  $\text{NaTiO}_x$  overlayer on Ru NPs does not affect the activation of  $\text{H}_2$  (small molecule gas can enter freely based on CO adsorption

and  $\text{H}_2$ -TPD experiments), but weakens the adsorption ability for LDPE (verified by butane-TPD) [3,12b]. The mechanism for hydrogenolysis of alkane C-C follows dehydrogenation and hydrocracking routes, so the decreased adsorbability for LDPE is advantageous to the cleavage of its internal C-C bonds [9a,9c,10a,32].

The effects of Ru loading, reaction temperature, reaction time, and  $\text{H}_2$  pressure on the conversion and selectivity are also investigated (Fig. 8). The conversion and liquid phase selectivity of Ru-supported NTO catalysts increase with Ru loading (Fig. 8a, Table S9). Higher (200 °C) reaction temperature did not improve the selectivity of the liquid products, and low temperature (< 180 °C) had poor conversion and liquid product selectivity (Fig. 8b, Table S10). LDPE can be completely converted after 8 h (Fig. 8c), and further prolonging the reaction time would reduce the reaction selectivity for high-value long-chain alkanes (Table S11). In the case of  $\text{Ru@NTO-NH}$ , the best



Scheme 1. Hydrogen hydrolysis of polyolefin long chain on  $\text{Ru@NTO-NH}$ .

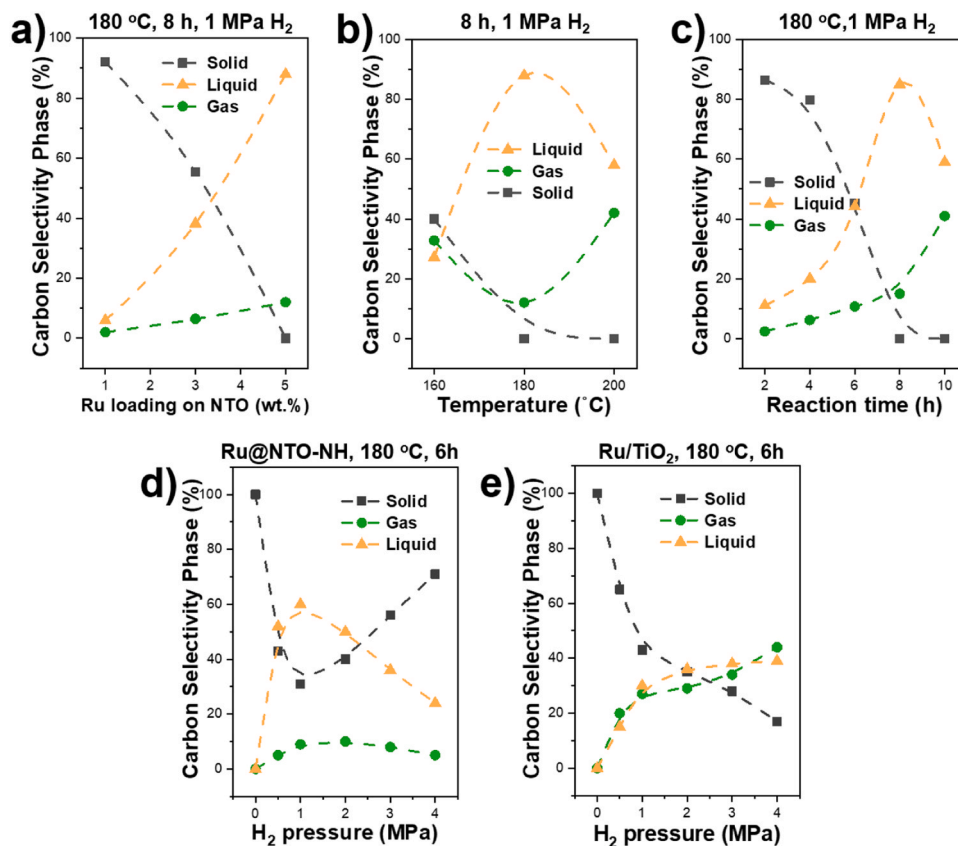


Fig. 8. The effects of (a) Ru loading, (b) reaction temperature, (c) reaction time, (d)  $\text{H}_2$  pressure on the  $\text{Ru@NTO-NH}$  catalyzed LDPE hydrogenolysis. (e) The effects of  $\text{H}_2$  pressure on the  $\text{Ru/TiO}_2$  catalyzed LDPE hydrogenolysis. Reaction condition: LDPE (500 mg), Ru catalyst (100 mg, 5 wt% of Ru).



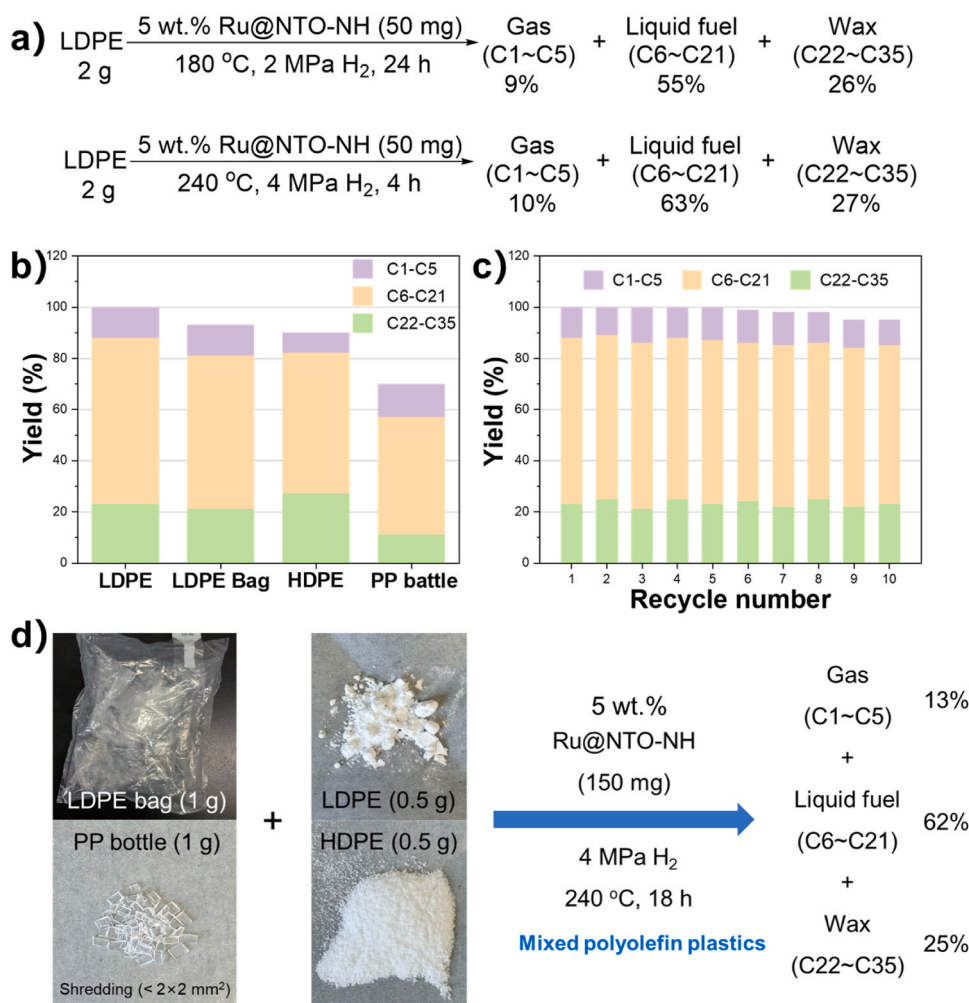
conversion and the liquid alkanes selectivity is observed under 1 MPa H<sub>2</sub> (Fig. 8d, Table S12). In contrast, the hydrogenolysis conversion of LDPE increases monotonously with hydrogen pressure in the same range of 0.5–4.0 MPa H<sub>2</sub> over Ru/TiO<sub>2</sub> (Fig. 8e, Table S13). The H<sub>2</sub> chemisorption equilibrium constant was calculated by the Langmuir equation. The H<sub>2</sub> chemisorption equilibrium constant of Ru@NTO-NH is about twice of Ru/TiO<sub>2</sub> at 50 °C (Fig. S8), demonstrating that the \*H binding energy on Ru@NTO-NH is stronger than Ru/TiO<sub>2</sub> under the same hydrogen pressure [10a]. The negative rate dependence on H<sub>2</sub> pressure on Ru@NTO-NH is attributed to its higher active H\* coverage than Ru/TiO<sub>2</sub> and the competitive adsorption of active H\* and alkyl chains [33].

According to the experimental, characterization and literature results [8,10,12a], the mechanism of PE hydrogenolysis on Ru@NTO-NH is illustrated in Scheme 1. (1) Although there are NaTiO<sub>x</sub> coatings on the surface of Ru NPs in the catalyst, it does not affect the adsorption of H<sub>2</sub> and PE chains, which is confirmed by H<sub>2</sub>- and *n*-butane-TPD results. Therefore, it is likely that the PE chains and H<sub>2</sub> are adsorbed and activated on the Ru NPs surface through the pore structure of the NaTiO<sub>x</sub> overlayer [8]. (2) The C-C bonds break into two alkyls adsorbed on the Ru sites under the synergistic action of the Ru catalytic center and H\*. The enhanced SMSI between Ru and NTO facilitates the formation of smaller, more positively charged Ru NPs, which enhances the H\* coverage on the catalyst surface, thereby promoting the internal C-C

bond cleavage step [10a]. (3) Alkane products are yielded by the alkyl hydrogenation process, following by alkane desorption from Ru NPs. The NaTiO<sub>x</sub>-coated Ru NPs weakens the adsorption ability of alkane molecules, which accelerates the alkane desorption steps, thus improving the selectivity of long alkane products [12b].

In order to further demonstrate the potential of Ru@NTO-NH, the scale-up LDPE hydrogenolysis (2 g) was performed (Fig. 9a). At 180 °C, LDPE could be completely converted within 24 h with a liquid selectivity of 91%. In addition, LDPE could be completely converted within 4 h at higher temperature (240 °C) and H<sub>2</sub> pressure (4 MPa) with 90% selectivity of liquid alkanes, which is better than most of previously reported Ru-based catalysts for LDPE hydrogenolysis (Fig. S9) [9a,10a, 10b,11,12a].

Encouraged by the remarkable results, Ru@NTO-NH was applied in the hydrogenolysis of other polyolefins, including LDPE plastic bags, HDPE, and PP (Fig. 9b, Table S14). The conversion rate of LDPE plastic bags reaches 93%. After increasing the temperature to 200 °C, the hydrogenolysis conversion of HDPE reaches 90%, and satisfactory selectivity for liquid fuel and wax is observed. The conversion of PP at 200 °C for 16 h is only 70% under identical conditions, but the selectivity for liquid fuel and wax is still good (77%). In order to simulate the hydrogenolysis of mixed plastics that actually exists in waste plastic treatment, gram-scale hydrogenolysis of commercial mixed waste polyolefin plastics is also carried out, which displays similar reactivity to



**Fig. 9.** (a) The scale-up LDPE hydrogenolysis. (b) Hydrogenolysis of LDPE, LDPE plastic bags, HDPE and PP with Ru@NTO-NH catalyst. Reaction condition: polyolefin (500 mg), 5 wt% Ru@NTO-NH (100 mg), 1 MPa H<sub>2</sub>, LDPE (180 °C, 8 h), LDPE bag (180 °C, 8 h), HDPE (200 °C, 8 h), PP (200 °C, 16 h). (c) Recyclability of Ru@NTO-NH. Reaction conditions: LDPE (500 mg), 5 wt% Ru@NTO-NH (100 mg), 180 °C, 8 h. (d) Hydrogenolysis of mixed polyolefin plastics with Ru@NTO-NH catalyst.

LDPE hydrogenolysis in a slightly longer reaction time (18 h), and the yield of liquid fuel and wax was 87% (Fig. 9d).

Finally, the recyclability of Ru@NTO-NH by hydrogenolysis of LDPE was investigated. After the reaction was completed, Ru@NTO-NH was filtered and washed, and directly reused for the next reaction cycle. As shown in Fig. 8b, only a minor loss in yield was observed after 10 runs, even there is a certain amount of catalyst loss (1–2 wt% each cycle) (Fig. 9c, Table S15). Furthermore, the used catalyst has been respectively characterized by XRD, TEM, HRTEM, XPS and ICP techniques to reveal the physical properties and the chemical environment at the catalyst interface. No Ru signal is observed in the XRD diagram of the used catalyst, which rule out the agglomeration of Ru particles during use (Fig. S5). TEM and HRTEM images show the NaTiO<sub>x</sub> overlayer still exists, but more severe aggregation and fracture of NaTiO<sub>x</sub> nanowires are observed (Fig. S10).

After 10 runs, there is almost no loss of ruthenium metal based on ICP results (Table S1). For the recycled catalyst, the peaks of Na 1 s and Ti 2p moved to high binding energies and the Ru 3d<sub>5/2</sub> peak shifted slightly to low binding energy owing to high temperature reduction reaction conditions. (Fig. S11). Furthermore, the residual low-molecular-weight polyolefins deposited on the Ru@NTO-NH catalyst after multiple catalytic cycles were investigated by O<sub>2</sub>-TPO. Compared with fresh Ru@NTO-NH, CO<sub>2</sub> was detected at different temperatures in the O<sub>2</sub>-TPO effluent of the catalyst recycled 10 times (Fig. S12). Therefore, electron transfer and carbon deposition may be responsible for the slight decrease in catalyst activity.

#### 4. Conclusions

In summary, this novel Ru@NTO-NH catalyst exhibits excellent activity for polyolefin hydrogenolysis due to the SMSI between Ru and NTO. Several characterizations and comparative experiments have been conducted, indicating that the NaTiO<sub>x</sub> overlayer derived from NTO effectively encapsulates the Ru nanoparticles (NPs) without impeding the adsorption of small gas molecules. Furthermore, the enhanced SMSI between Ru and NTO facilitates the formation of smaller, more positively charged and NaTiO<sub>x</sub>-coated Ru NPs. This structural feature enhances the H\* coverage on the catalyst surface and weakens the adsorption ability of alkane molecules, thereby leading to excellent catalytic performance in polyolefin hydrogenolysis with high selectivity. The Ru@NTO-NH catalyst also exhibits impressive conversion and selectivity towards long-chain alkanes in the hydrogenolysis of HDPE, PP, and real LDPE plastic bags. Additionally, it demonstrates excellent stability and recyclability, as evidenced by negligible activity degradation even after 10 reaction cycles. This novel conformational relationship between catalyst structure and function exposes exciting opportunities to engineer plastic recycling and upcycling.

#### CRediT authorship contribution statement

**Xueping Zhang:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Quan Gan:** Investigation, Data curation. **Peng Zhou:** Writing – review & editing. **Zhong Chen:** Writing – review & editing. **Zehui Zhang:** Writing – review & editing. **Guo-Ping Lu:** Conceptualization, Formal analysis, Writing – review & editing, Supervision, Funding acquisition.

#### Declaration of Competing Interest

There are no conflicts to declare.

#### Data availability

No data was used for the research described in the article.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123626.

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